

Specific Reduction Behavior of Nitoraceophenone in Acetonitrile using Flow Electrolysis-ESR Spectroscopy

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We have studied of the substituent effects such as electron-withdrawing or electron-donating substituents on the electroreduction processes of acetophenone (AP) derivatives in acetonitrile by using a flow-electrolysis-ESR measurement. Flow electrolysis-ESR spectroscopy has allowed the rapid and quantitative electrolysis, so the ESR spectra of the short lived radical ions can be easily observed. The carbonyl carbon radicals were generally generated by the reduction of carbonyl group in the reduction processes of acetophenone derivatives. In this studies, we found the specific reduction behavior of p-nitroacetophenone; that is the electron transfer site changed from that of the other AP derivatives, and the nitrogen radical was generated from the reduction of nitro group.

In the CV of AP in AN, an one-electron irreversible cathodic peak due to the electrogeneration of the anion radical ($AP^{\bullet-}$) was observed at -2.35 V. In the anodic scan, a small anodic peak was observed, it could be inferred that following chemical reaction of $AP^{\bullet-}$. In the CV of p-cyanoacetophenone (CAP), a reduction peak due to the generation of its anion radical shifted to positive potential than that of acetophenone and its reoxidation peak shows a slightly reversible electron transfer reaction. That is to say, by the substituent effects of electron withdrawing cyano group, the reduction of acetophenone become easier and the generated anion radicals become more stable. On the contrary, in the CV of p-methoxyacetophenone (MOAP), a reduction peak due to the generation of its anion radical shifted to negative and the intensity of its reoxidation peak decreased by introducing an electron donating methoxy group. That is, owing to the substituent effects of the electron donating methoxy group, the reduction of acetophenone became a little difficult and the generated anion radicals became more unstable.

The S/N ratio in the ESR spectrum of CAP increased than that of AP, which shows the CAP anion radical became more stable owing to the electron withdrawing effect of cyano group. The ESR spectrum of CAP anion radical became somewhat broaden, which showed the decreasing effect of an electron withdrawing cyano group on the double bonding tendency between benzene ring and the carbon in a carbonyl group.

In contrast, in the CV of NAP, two reduction peaks were observed at -1.17 V and -1.75 V. These peaks are corresponding to the formation of the NAP anion radical and the NAP dianion, respectively. While in the reversed oxidation scan, two additional oxidation peaks were appeared at more positive potentials than those of the normal two reversible oxidation peaks. From these results, it can be inferred that, in the case of NAP dianion, unpaired electrons localized to form two different states. As the results of the flow electrolysis-ESR measurements, we could successfully observed the ESR spectra at the first and the second reduction peak regions by controlling the applied potential on the column electrode. While the g-value of the anion radical of AP derivatives was 2.0033, the g-value of the NAP anion

radical was remarkably large as $g = 2.0049$. This shows the unpaired electron of the NAP anion radical localized on N atom. While at the second reduction peak region, a different ESR spectrum was observed having a g-value of 2.0073, which is larger than that of the NAP anion radical. From these results, it seems that the NAP dianion has paramagnetic character and the electron localizes on O atom. As a result, it can be concluded that the paramagnetic NAP dianion with biradical form is produced at the second reduction peak region and the unpaired electrons localize at two atoms; one is at the C atom bonding to the nitro group, the other is at the O atom of the carbonyl group.

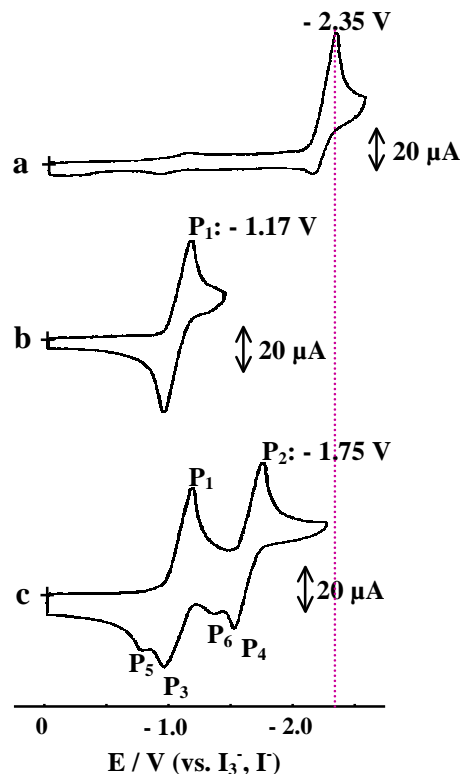


Figure 1. CV responses of 1.0 mM of (a) AP, (b) and (c) p-NAP in 0.1 M TBAP with the GC disk electrode. The scan rate was 200 mV/sec.

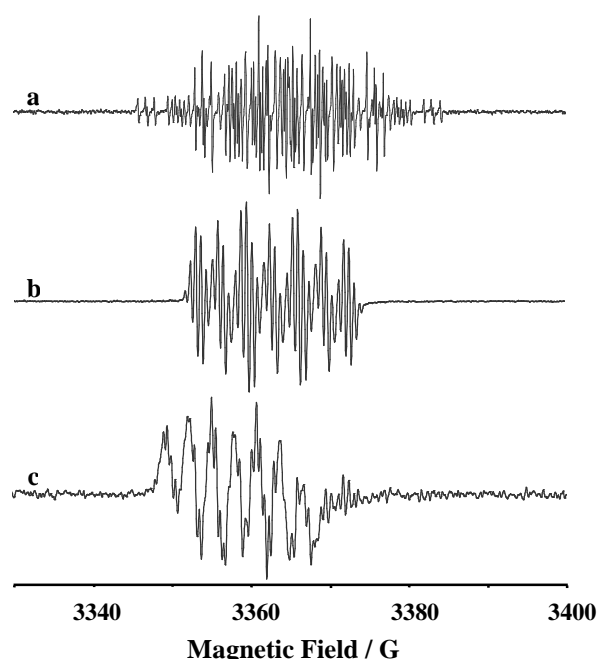


Figure 2. ESR spectra of p-NAP reduction species: (a) AP anion radical ($AP^{\bullet-}$), (b) p-NAP anion radical ($NAP^{\bullet-}$), and (c) p-NAP dianion.